

# A passive regulated thermal gradient device and application to unpowered refrigeration and heating

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We describe a device which uses a thermodynamically favorable process to generate a sustained temperature gradient in the absence of input of any but ambient thermal energy. A particular constructed prototype creates a temperature gradient of  $2.5^{\circ}C$ , and may be combined to generate batteries of the device. One such two-unit battery generates a  $5.7^{\circ}C$  temperature difference. The device may be “recharged” using only ambient thermal energy and does not require fossil, electrical, mechanical, or other generated power.

**Keywords:** saline gradient, refrigeration, heating

## 1 Introduction

Refrigeration mechanisms most often function by making a working fluid cold in one region to absorb energy and warm in another region to expel energy[1]. The combination of these processes generates an energy flow but also require external energy to function. In this paper we describe a system in which the flow of thermal energy is produced by a thermodynamically favorable process, and the energy being moved *itself* drives the process.

This paper examines the use of a property of solutions in generating a flow of energy from one solution to another. We first illustrate theoretically why an equilibrium state is reached in which a temperature difference is generated. We then describe a single and multi-unit device that generates the thermal gradient and maintains it for some time. Finally, we examine the expected energy absorption per unit in multi-unit devices.

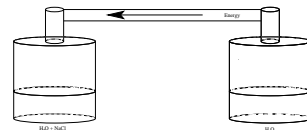
## 2 Salinity gradients

It is well known that high salinity water has a lower vapor pressure than low salinity water[2, 3, 4]. As the vapor moves from one water body to another of different salinity, it carries with it heat, moving heat from the body of water with the lower salinity to that with the higher salinity. This transport of thermal energy continues as long as the vapor pressures of the two water bodies differ. As the side with the lower salinity is continually getting colder, and the side with the higher salinity is continually getting warmer, the two vapor pressures will eventually become equal. At this

point, the system reaches an equilibrium state with the higher salinity side at a higher temperature than the lower salinity side.

The process generally happens slowly enough that the temperature difference is easily overwhelmed by thermal leakage. In the presence of a good design and insulation, the leakage can be limited, and the temperature difference can become sizeable.

We examine the behavior of a salinity difference device, as shown in Figure 1. We assume that the device is surrounded by a heat reservoir at temperature  $t_R$ . Moreover, we assume that the device is made from a material which is impervious to heat (a perfect thermal insulator) except for the tanks of water. We assume that the tanks are made of a thermally conductive material (however slow) and that some surface area is exposed to the external reservoir. On one end is a tank filled with distilled water. The tank has an external area in contact with the external reservoir  $A_R$ . We assume that the surface of the water has area  $A_c$ . On the other end is a second tank with external surface area  $A_{R'}$  and filled with saline water. The saline water, we assume, has a surface with area  $A_h$ . We assume a tube connects the distilled water tank with the saline water tank. We also assume that the entire device is filled with only water vapor; no other gas is in the device.



**Figure 1:** A simplified salinity gradient device. <sup>1</sup>

<sup>1</sup>A version of this device was used by [5] to generate

Generally, as long as the pressure above the distilled water is lower than its equilibrium pressure, water will evaporate from the distilled water tank. It can be shown that to a good approximation the rate at which the water vapor flows out of the distilled water tank is [6]

$$R_c = A_c \alpha (\phi_d(t_c) - \phi'_d(t_c)) \quad (1)$$

where  $A_c$  is the surface area of the distilled water tank,  $t_c$  is the temperature of the distilled water,  $\phi_d(t_c)$  is the equilibrium vapor pressure of the distilled water at temperature  $t_c$ ,  $\phi'_d(t_c)$  is the actual vapor pressure above the distilled water at temperature  $t_c$ , and  $\alpha$  is a proportionality constant given in  $\frac{\text{moles}}{\text{m}^2 \cdot \text{atm} \cdot \text{s}}$ . Likewise, the rate at which the water flows out of the saline water tank is

$$R_s = A_h \alpha' (\phi_s(t_h) - \phi'_s(t_h)) \quad (2)$$

where  $A_h$  is the surface area of the saline water tank,  $t_h$  is the temperature of the saline water,  $\phi_s(t_h)$  is the equilibrium vapor pressure of the saline water at temperature  $t_h$ ,  $\phi'_s(t_h)$  is the actual vapor pressure above the saline water at temperature  $t_h$ , and  $\alpha'$  is a proportionality constant. Note that  $\phi'_s(t_h)$  is generally higher than  $\phi_s(t_h)$  and so the vapor is being absorbed by the water. Note also that  $\alpha'$  is a function of the concentration of salt in the saline water. We assume for the moment that the concentration of salt in the saline water is constant.

It is straightforward to show that in equilibrium, the density of water vapor along a one-dimensional tube between the distilled and saline tanks is

$$\phi(x) = \phi'_d(t_c) - x \frac{\phi'_d(t_c) - \phi'_s(t_h)}{L} \quad (3)$$

where  $\phi'_d(t_c)$  is the vapor pressure of water above the distilled water tank at the colder temperature  $t_c$  and  $\phi'_s(t_h)$  is the vapor pressure above the salt water at the high temperature  $t_h$ . The rate at which the vapor moves along the gradient is equal to

$$J = -D \frac{\partial \phi}{\partial x} = \frac{D}{L} (\phi'_d(t_c) - \phi'_s(t_h)) \quad (4)$$

where  $D$  is the diffusion constant of the vapor in units of  $\frac{\text{moles} \cdot \text{m}}{\text{atm} \cdot \text{s}}$ . Outside of any transient fluid flow, we have that

$$J = R_c = R_s. \quad (5)$$

Then it can be shown that

$$\phi'_s(t_h) = \frac{(A_c L \alpha - D) A_h \alpha' \phi_s(t_h) - D A_c \alpha \phi_d(t_c)}{L A_h A_c \alpha \alpha' - D (A_h \alpha' + A_c \alpha)} \quad (6)$$

and

$$\phi'_d(t_c) = \frac{(A_h L \alpha' - D) A_c \alpha \phi_d(t_c) - D A_h \alpha' \phi_s(t_h)}{L A_h A_c \alpha \alpha' - D (A_h \alpha' + A_c \alpha)}. \quad (7)$$

electricity.

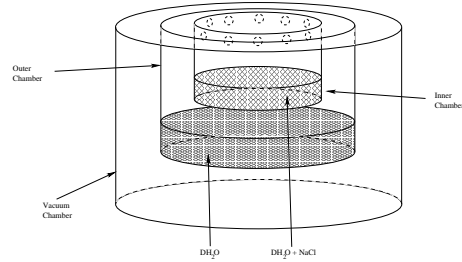
Vapor stops flowing out of the distilled water tank when  $\phi_d(t_c) = \phi'_d(t_c)$ . This will happen in the general case when  $\phi_d(t_c) = \phi_s(t_h)$ . The temperatures for which this occurs must be empirically determined. It is clear, however, that due to the colligative vapor pressure reduction of the fluid,

$$t_h > t_c. \quad (8)$$

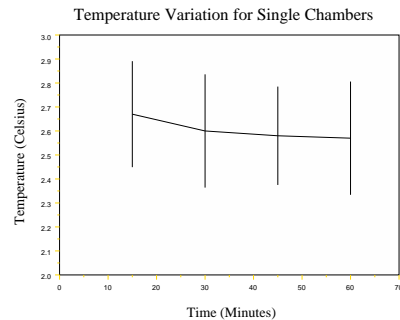
Equation (8) establishes that the temperature must be different in the two chambers in equilibrium. The effect is generally masked by thermal leakage in practical application. However, careful construction of a device allows for the measurement of this temperature difference.

### 3 A thermal gradient device

We constructed a nested two-chamber device illustrated in Figure 2. entirely from acrylic plastic. Distilled water is in the outer chamber while salt water is found in the inner chamber. The inner chamber has holes cut into it so as to allow vapor to move between chambers.



**Figure 2:** A single chamber nested device. One chamber holds distilled salt water ( $DH_2O$ ) and the other holds water and salt, in this case  $NaCl$ .



**Figure 3:** The evacuation of air excluding water vapor in the chamber generates conditions under which the temperature difference equilibrates and becomes maintained at  $\sim 2.5^\circ C$ . We illustrate the first hour of evacuation of the chamber

The entire device is encapsulated by a third chamber. The space between the larger chamber and the  $DH_2O$  chamber contains a high vacuum, insulating

the chambers from external energy leakage. The top cap of the device seals both the  $H_2O + NaCl$  chamber and the  $DH_2O$  chambers, and it is in contact with the external environment. The device becomes “active” when the space between the  $DH_2O$  and the  $H_2O + NaCl$  is evacuated of its air, and the air is replaced with water vapor. The device is sealed in this state, and allowed to “run”. Under these conditions, the device achieves a temperature difference and maintains it, as can be seen in Figure 3.

It is interesting to ask how much water need be transferred from one chamber to the other in order to create a temperature difference like that in Figure 2. Energy is transferred through the evaporation and condensation of water vapor. The evaporation of one mole of water carries with it the molar heat of vaporization. We denote the heat of vaporization by  $E_v$ .

The temperature change in the water in the distilled tank after evaporation of a volume given by  $\delta V$  is

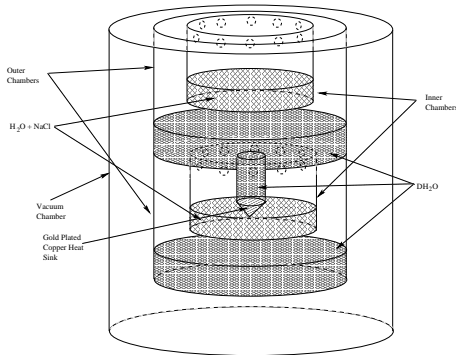
$$\Delta T = \frac{E_v}{C_v} \ln \left( 1 - \frac{\delta V}{V_i} \right) \quad (9)$$

where  $C_v$  is the specific heat and  $V_i$  is the initial volume of the water. Inverting this equation, we have

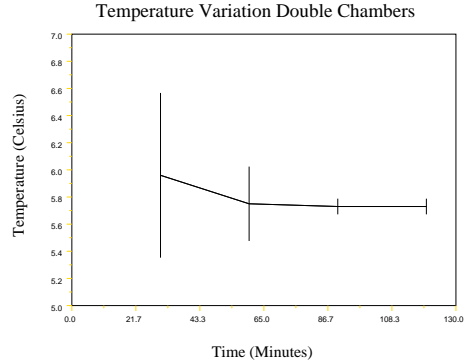
$$\delta V = V_i \left( 1 - e^{-\frac{\Delta T C_v}{E_v}} \right). \quad (10)$$

If we then wanted to reduce the temperature of the water by  $2.5^\circ C$ , this would require a reduction in temperature of 0.45%. Thus, creating the temperature difference observed in the single chamber requires only a movement of 0.45% of the water, assuming that the salt tank’s temperature is stabilized.

We would like to be able to generate a temperature difference greater than  $2.5^\circ C$ . We do this by creating batteries of individual units. Suppose that we have two devices as shown in Figure 4.



**Figure 4:** A two-chamber battery. The design is an extended version of the single-chamber system. Two chambers identical to the initial design are placed one above the other with the top chamber’s distilled reservoir in thermal contact with the bottom chamber’s salt reservoir.



**Figure 5:** When utilized over an extended period of time, the temperature differential holds steady at  $5.7^\circ C$ . We illustrate the first two hours after evacuation of the chambers.

The bottom chamber is identical to the single chamber system. The top chamber has an acrylic tube which extends the lower  $DH_2O$  tank added to the bottom chamber and into the salt tank of the lower chamber. This facilitates heat transfer between the two chambers. A copper bar which has been coated in gold<sup>2</sup> seals the end of the tube. This transfers heat from the lower chamber to the upper chamber, synchronizing their temperatures. It is straightforward to show that the total temperature difference between the lower distilled water and the upper salt solution tank is greater than that of the single chamber, with the difference of each chamber being added together. We have found that, with two chambers, the temperature difference is  $5.7^\circ C$  (Figure 5).

It is also evident that the evaporation and condensation events occur at the surface of water in either tank. In the distilled water tank, it is an evaporation event, which absorbs energy, cooling the surface. Since the surface is naturally cooled, convection mixes the cooled water with the warmer water below. On the other hand, the condensation, which also occurs at the surface of the salt water, naturally brings heat to the surface of the water. The salt water does not mix readily so the heat tends to stay at or near the surface.

The design in Figure 4 allows absorbed heat from the lower chamber’s salt water tank to transfer through the copper plug into the upper chamber’s distilled water tank. The higher temperature water rises, naturally mixing with the cooler water from above. Simultaneously, as the water on the top of the upper distilled water tank cools, the cooled water descends, mixing with the warmer water below, which rises to the surface. As a result, the heat from the lower salt chamber is naturally absorbed by and mixed in the upper distilled water chamber.

<sup>2</sup>The gold plating is simply a measure used to protect against corrosion[7].

## 4 Consumption

One of the important aspects of moving energy through the system in this way is the fact that, if the salt solution tank contains salt crystals then some of the the energy must be used to dissolve some of the salt. *This entropy-increasing effect is what drives the system, thermodynamically, and makes it spontaneous.* This represents a sink in the system which absorbs heat rather than carrying it out of the system.

Suppose  $\Delta E$  is emitted from the water tank through evaporation of a quantity of water. The quantity of water is  $n = \frac{\Delta E}{E_v}$  where  $\Delta E$  is Joules, and  $E_v$  is given in  $\frac{J}{mol}$ . This amount of water (in moles) is deposited in the salt water tank, where the energy is absorbed by the water. If the salt dissociation is governed by the equilibrium equation  $AB \rightleftharpoons A + B$  and if the solubility constant is given by  $K_{sp}$  we have that

$$\frac{M_m \Delta E \sqrt{K_{sp}}}{\rho E_v} = moles_{Na}. \quad (11)$$

The dissolution energy of salt crystal absorbs energy, as it is slightly endothermic. As a result, the amount of energy left for heating is given by

$$\Delta E \left( 1 - \frac{M_m G \sqrt{K_{sp}}}{\rho E_v} \right) = E_G \quad (12)$$

where  $G$  is the molar Gibbs free energy of dissolution,  $\rho$  is the density of the solvent, and  $M_m$  is the molar mass of the solvent. For water at  $25^\circ C$ ,  $E_G = 0.9773 \Delta E$ . Thus, we may expect this much energy to contribute to heating the salt water, or to be moved through the next stage. If we have an  $N$ -stage battery, we can estimate the amount of energy absorbed while going through the battery as <sup>3</sup>

$$\Delta E \left( 1 - \frac{M_m H \sqrt{K_{sp}}}{\rho E_v} \right)^N = E_{h,N}. \quad (13)$$

This is a drop of approximately  $0.168 \Delta E$  for an eight chamber system (enough for a  $24^\circ C$  temperature drop), leaving more than  $0.832 \Delta E$  to move through the system. The calculation of similar values for different substances than  $H_2O$  and  $NaCl$  is straightforward.

## 5 Discussion and conclusion

The device described above is based on the observation that differing solution concentrations tend to

<sup>3</sup>This approximation is not strictly true as  $K_{sp}$  is temperature dependent. A more careful analysis would take into account the temperature variations, and would report this number for various temperature ranges. However, this is beyond the scope of the present study.

cause differing vapor pressures, which can, in turn, generate vapor flows. This vapor flow causes a movement of thermal energy which itself generates a sustained and sustainable thermal gradient between two parts of a system spontaneously. We have used this to generate sustained thermal gradients in single unit and multi-unit devices, using salt and water, both of which are plentiful and readily available.

In our study, the equilibration time of the two stage device is about 90 minutes. However, as the effect can be expected to be a function of the surface area of the distilled and saline reservoirs, it is expected that the equilibration time could be significantly improved. In our devices, the surface area of the distilled water is  $31.65 \text{ cm}^2$  while that of the saline water is  $11.39 \text{ cm}^2$ . Devices suitable for residential or commercial use might easily be developed with much larger surface areas and concomitantly much quicker equilibration times. It is also interesting to ask what the increase in equilibration time is with increased numbers of chambers. This is a subject of future study.

One of the limitations of the current device, which uses water and salt, is that the device cannot cool to temperatures below  $0^\circ C$ . This is a natural consequence of the fact that the vapor pressure of water at  $0^\circ C$  is zero, and so no movement of energy is possible. As a result, freezing cannot be done with water alone. Moreover, heating of a chamber when the exterior temperature is below  $0^\circ C$  is also impossible using salt and water alone. Utilizing different solvents such as methanol or ethanol may extend the usable temperature range of such a device. This is the subject of future research.

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